

Claim 1. A method to determine the best fit parameters of a broadening model to be used to correct for the effects of band broadening in a chromatographic separation containing a separation device followed by two or more detectors comprising the steps of

- a) Selecting a broadening model containing a set of adjustable parameters;
- b) Injecting a sample containing a monodisperse component;
- c) Collecting the signals from each of said detectors corresponding to said monodisperse component;
- d) Forming a χ^2 model to be minimized over the peak of said monodisperse component using said collected signal of the most broadened detector signal as a reference against which the said other detector signals are to be broadened;
- e) Minimizing the χ^2 model to determine said best fit parameters for each of said detector signals to be broadened so that their broadened and normalized shapes are a best fit to said shape of said detector producing said broadest temporal response.

Claim 2. The method of Claim 1 where the minimization of said χ^2 model is achieved by use of a nonlinear least squares algorithm.

Claim 3. The method of Claim 2 where said nonlinear least squares algorithm is of the type developed by Marquart.

Claim 4. The method of Claim 1 where said χ^2 model to be minimized is

$$\chi^2_i(\beta_i, \tau_i, \alpha_{ij}) = \int_{peak} \left(D_n(t) - \beta_i \int_{-\infty}^{\infty} D_i(t-\tau) B(\alpha_{ij}, \tau - \tau_i) d\tau \right)^2 dt, \text{ where said best fit parameters}$$

are the β_i, α_{ij} , and τ_i ; the i -detectors' responses as a function of time are the $D_i(t)$; and said model is minimized over said peak.

Claim 5. The method of Claim 1 where said band broadening is caused by dilution.

Claim 6. The method of Claim 1 where said broadening is caused by mixing.

Claim 7. The method of Claim 6 where said mixing arises from inclusions caused by mechanical defects within the detector cells and/or connectors therefore.

Claim 8. The method of Claim 1 where said broadening is caused by internal instrumental effects.

Claim 9. The method of Claim 8 where said internal instrumental effects are caused by electronic filtering.

Claim 10. The method of Claim 8 where said internal instrumental effects are caused by differences of the sample volume measured by each detector.

Claim 11. A method to derive selected physical properties of a sample passing successively through a set of detectors using a combination of the signals produced by said detectors responding to said sample passing therethrough when some of said detectors exhibit band broadening of their signals, comprising the steps of

- 1 a) Applying a parameterized broadening function to said detector set to derive thereby a
2 corresponding set of detector signals, all of which have comparable broadening; and
3 b) Using said detector signals now broadened, following application of said broadening
4 function, to derive said selected physical properties of said measured sample.

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6 **Claim 12.** The method of Claim 11 where said application of said parameterized broadening
7 function is given by $D_i^b(t) = \int_{-\infty}^{\infty} D_i(t-\tau) B(\alpha'_{ij}, \tau - \tau'_i) d\tau$ where $D_i^b(t)$ are the said detector
8 signals now broadened, α'_{ij} and τ'_i are said best fit parameters of Claim 2.

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10 **Claim 13.** The method of Claim 11 where said selected physical properties, to be determined
11 from the relation $R(\theta) = K^* M_w c P(\theta) [1 - 2 A_2 M_w c P(\theta)] + O(c^3)$, are the weight averaged molar
12 mass, M_w , and the root mean square radius, r_g , of said sample derived from concentration
13 signals, $c(t)$, and the excess Rayleigh ratios, $R(\theta, t)$, derived from i light scattering signals from
14 a detector set comprised of light scattering detectors, $D_i(t)$, and a dRI detector in sequence, said
15 dRI detector producing a concentration signal exhibiting broadening relative to said light
16 scattering detector signals, where said light scattering detector signals have been broadened.

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18 **Claim 14.** The method of Claim 11 where said detector signals are from a UV detector followed
19 by a multiangle light scattering detector and said multiangle light scattering signals are
20 broadened.

1 Claim 15. The method of Claim 11 where said detector signals are from a refractive index
2 detector followed by a viscometer detector and said refractive index detector signals are
3 broadened.

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5 Claim 16. The method of 11 where said broadening function is given by

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$$B(t) = \int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} e^{-\tau^2/2\sigma^2} \frac{1}{w} U(t-\tau) e^{-(t-\tau)/w} d\tau, \text{ where } U(t-\tau) = 1 \text{ when } t \geq \tau \text{ and } = 0 \text{ when } t < \tau.$$

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8 Claim 17. The method of Claim 16 where said optimal parameters of said broadening function
9 have been determined by the method of Claim 1.

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11 Claim 18. A method to determine the delay volumes, τ_i , $i = 1$ to $N-1$, between N detectors in a
12 chromatographic separation system using the method of Claim 2.